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THE Be-Mo (BERYLLIUM-MOLYBDENUM) SYSTEM

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Equilibrium Diagram

[73Gol] tentatively composed the Be-Mo phase diagram from various results reported in [Hansen] and [Elliott]. Thermodynamic modeling by [80Bre] nearly reproduced the diagram of [73Gol], with only significant change in the extended stability of $Be_{22}Mo$ at low temperatures. The assessed diagram (Fig. 1) is primarily adopted from [80Bre], with some modification based on experimental observations.

There are four intermediate phases reported for this system: (1) $Be_{22}Mo$ ($Zn_{22}Zr$-type); (2) $Be_{12}Mo$ ($Mn_{12}Th$-type); (3) Be_2Mo ($MgZr_2$-type); and (4) $BeMo_3$ (Cr_3Si-type). The melting points and the homogeneity ranges for all phase compounds have not been well established.

(βBe) and (αBe) Terminal Solid Solutions. The melting point of βBe and the βBe --> αBe allotropic transformation temperature are 1289±4 and 1270±6 °C, respectively [86BAP]. The reaction type between (βBe) and (αBe) and the solubility limits of Mo in these terminal solid solutions have not been reported.

(Mo) Terminal Solid Solution. The melting point of Mo is 2623 °C [Melt]. The Mo solvus was deduced from hardness measurements by [51Ham]:

Temperature, °C	at.% Be
eutectic	0.53
1740	0.42
1480	0.2

Earlier, [50Ham] estimated the solubility limit of Be in (Mo) to be about 0.9 at.%. A eutectic structure composed of (Mo) plus Be_2Mo was observed beyond the solid solubility [50Ham, 50Kau]. The eutectic composition is at approximately 57 at.% Mo according to microstructural examinations [51Ham]. Observations of incipient melting by [51Ham] placed the eutectic temperature slightly below 1870 °C. [80Bre] estimated this temperature to be at 1827±50 °C.

$Be_{22}Mo$. The existence of and the formula for this compound were established by [61Boo], [62Mat], [63Kri], and [64Mat], replacing earlier tentative stoichiometries of $Be_{25}Mo$ [59Arz1, 59Arz2] and $Be_{20}Mo$ [60Pai]. Diffusion studies suggested the existence of this phase at temperatures between 1050 and 1200 °C, but not at 950 °C [59Arz1] nor at room temperature [60Zal].

The superconducting transition temperature of $Be_{22}Mo$ has been reported to be 2.51 K by [67Buc] and 2.545 K by [73Mat].

$Be_{12}Mo$. This phase was initially identified as $Be_{13}Mo$ by [36Mis] and [51Gor]. The more satisfactory stoichiometry was determined by [51Ham] and later confirmed by many other investigators, viz. [55Rae], [57Gla], [58Che], [59Arz2], [60Zal], [62Mat], [64Mat], and [65Bea]. The melting point is approximately 1700 °C [60Sto].

Be_2Mo. This phase was first observed by [36Mis], and subsequent reports by [51Gor], [59Pai], [60Zal], [62Mat], and [64Mat] confirmed its existence. The melting point (T_m) of Be_2Mo was set at 1840 °C by [59Pai]. The thermodynamic model by [80Bre] places T_m at a somewhat higher temperature (2027±200 °C), as [73Gol] assumed, in order to be consistent with the observed L —> Be_2Mo + (Mo) eutectic point.

The superconducting transition temperature for Be_2Mo is 1.68 K [73Mat].

$BeMo_3$. This phase was reported by [59Pai] and believed to melt at >1650 °C. However, this compound must decompose by a solid state reaction at a high temperature in order to be consistent with presence of the established eutectic between (Mo) and Be_2Mo. [80Bre] estimated a peritectoid reaction with a temperature at 900±100 °C. We have indicated this reaction to be at 1650 < T < 1827 °C.

Metastable Phase

[80Tan] predicted the possible existence of a metastable phase, BeMo, having the CsCl-type crystal structure from the study of a series of Be-transition metal systems.

Crystal Structures

A summary of crystal structure and lattice parameter data is given in Table 1. The mean linear thermal expansion coefficient of $Be_{12}Mo$ was measured by [65Bea].

Mean linear thermal expansion coefficient of $Be_{12}Mo$ [65Bea].

Temperature, °C	α, $x10^{-6}m/m/°C$
27 to 316	12.1
27 to 982	15.1
27 to 1482	16.7

Thermodynamics

[80Bre] calculated a Be-Mo phase diagram (Table 2) based on estimated thermodynamic functions for various Be-Mo phases as given in Table 3. His calculated liquidus boundaries are accepted in Fig. 1. The $Be_{22}Mo$ and the $BeMo_3$ phases were proposed to be stable below 1300 and 900±100 °C, respectively. The low-temperature instability of $Be_{22}Mo$ in Fig. 1 is, however, based on experimental observations.

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* Indicates key paper.
# Indicates presence of a phase diagram.

Acknowledgments

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Table 1 Be-Mo Crystal Structure and Lattice Parameter Data

Phase	Composition, at.% Mo	Pearson symbol	Strukturbericht designation	Space group	Prototype	Lattice parameters, nm a	c	Reference
(βBe)....	0	cI2	A2	Im3m	W	0.25515	...	[82Kin]
(αBe)....	0	hP2	A3	$P6_3/mmc$	Mg	0.22857	0.35839	[81Kin]
$Be_{22}Mo$...	4.3	cF184	...	Fd3m	$Zn_{22}Zr$	1.1636	...	[62Mat]
						1.1634	...	[63Kri]
$Be_{12}Mo$...	7.7	tI26	$D2_b$	I4/mmm	$Mn_{12}Th$	0.7271	0.4234	[55Rae]
						0.7255	0.4188	[57Che]
						0.7286	0.4242	[57Gla]
						0.7252	0.4232	[58Che]
						0.7285	0.4264	[59Arz2]
						0.7251	0.4234	[84Col]
Be_2Mo....	33.3	hP12	C14	$P6_3/mmc$	$MgZr_2$	0.4444	0.7290	[36Mis]
						0.4433	0.7341	[51Gor]
	32.89					0.4449	0.7298	[75Stu]
	33.27					0.4442	0.7294	
	33.33					0.4448	0.7310	
$BeMo_3$....	75	cP8	A15	Pm3n	Cr_3Si	0.489	...	[60Pai]
(Mo)....	100	cI2	A2	Im3m	W	0.31470	...	[81Kin]

Table 2 Phase Boundaries Estimated by [80Bre]

Boundary	Type	Expression
L/[L+(Mo)]	Liquidus	$X_{Be} = 5.84\times10^{-4}(2890-T) - 9\times10^{-10}(2890-T)^2 - 7.5\times10^{-11}(2890-T)^3 \pm 0.01$
[L+(Mo)]/(Mo)	Solidus	$X_{Be} = 1.86\times10^{-5}(2890-T) - 2.08\times10^{-8}(2890-T)^2 + 7\times10^{-12}(2890-T)^3 \pm 0.001$
(Mo)/[(Mo)+Be_2Mo]	Solvus	$X_{Be} = -11000/T \pm 0.1$
L/[L+Be_2Mo]	Liquidus (Mo-rich)	$X_{Be} = 0.425+1.09\times10^{-3}(T-2100)-7.9\times10^{-6}(T-2100)^2 + 4.2\times10^{-8}(T-2100)^3 \pm 0.02$
L/[L+Be_2Mo]	Liquidus (Be-rich)	$X_{Be} = 0.991 - 1.5\times10^{-3}(T-1900)+6.7\times10^{-6}(T-1900)^2 - 1.24\times10^{-8}(T-1900)^3 \pm 0.04$
L/[L+$Be_{12}Mo$]	Liquidus (at high X_{Be})	$\ln X_{Mo} = -9.64+2.7\times10^{-2}(T-1500)+6.7\times10^{-5}(T-1500)^2 + 7.9\times10^{-8}(T-1500)^3 \pm 0.02$

X in atomic fraction. T in K.

Table 3 Thermodynamic Data Estimated by [80Bre]

For Mo(l) = Mo(liq.soln.)

$\bar{G}^{ex}/RT = (0.5 - 2060/T)X_{Be}^2 \pm 0.3$ (1300 to 2890 K)
and the corresponding equation for Be.

For Be(s) = Be(bcc Mo)

$\bar{G}^{ex}/RT = 8600/T \pm 0.2$ (2100 to 2890 K)

For Be(s) + 3Mo(s) = $BeMo_3$(s)

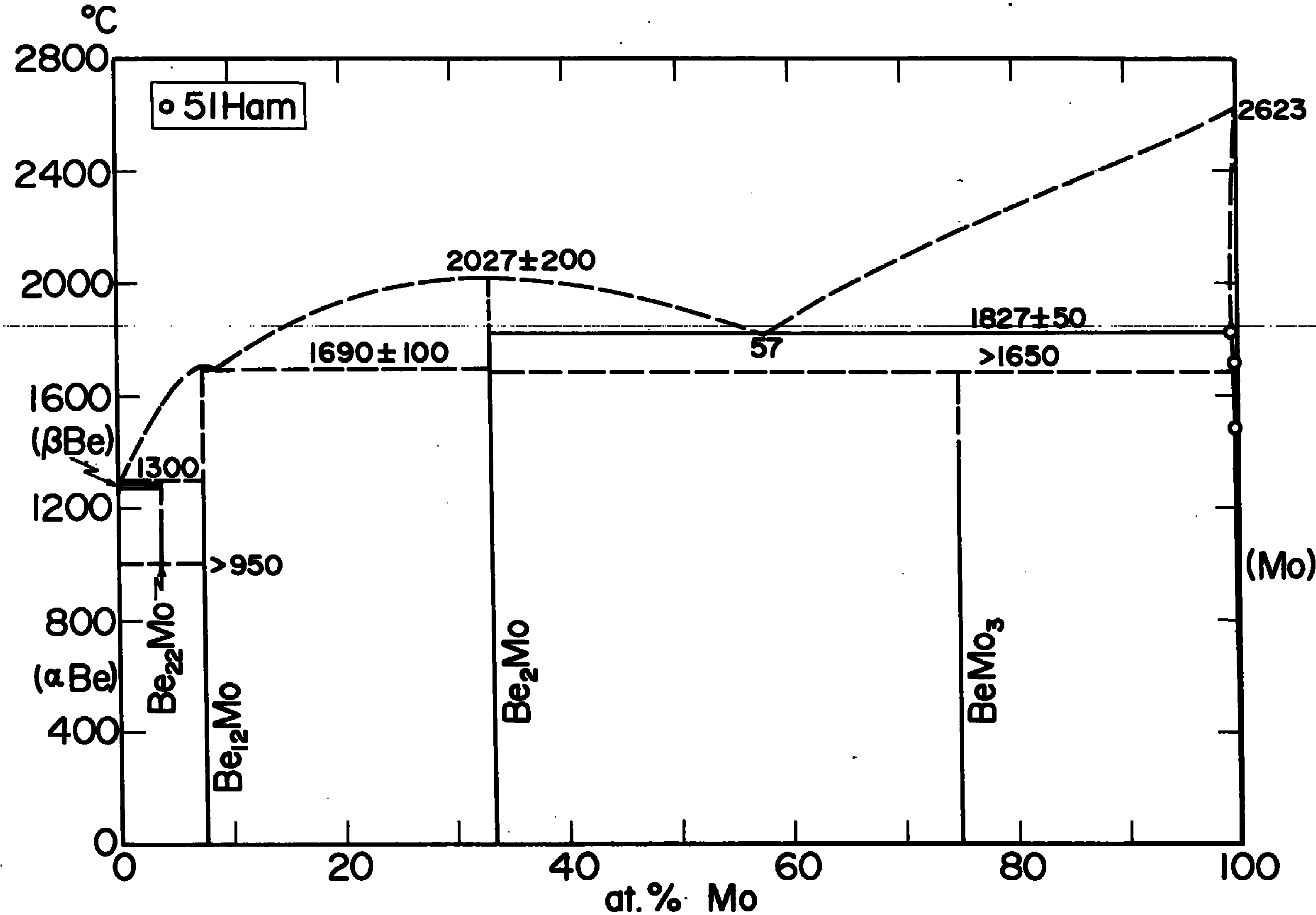
$\Delta H_{298}^{\circ}/R = -2200 \pm 2000$ K
$(G^{\circ} - \Delta H_{298}^{\circ})/RT = 0.9 \pm 0.5$ (298 to 900 K)

For 2Be(s) + Mo(s) = Be_2Mo(s)

$\Delta H_{298}^{\circ}/R = -3800 \pm 2000$ K
$(G^{\circ} - \Delta H_{298}^{\circ})/RT = 0.79 \pm 0.5$ (298 to 2027 K)

For 22Be(s) + Mo(s) = $Be_{22}Mo$(s)

$\Delta H_{298}^{\circ}/R = -13000 \pm 2000$ K
$(G^{\circ} - \Delta H_{298}^{\circ})/RT = -1 \pm 2$ (198 to 1570 K)



°C
2800
2400
2000
1600
1200
800
400
0
o 51Ham
2623
2027±200
1827±50
57
1690±100
>1650
(βBe)
1300
>950
(Mo)
(α Be)
$Be_{22}Mo$
$Be_{12}Mo$
Be_2Mo
$BeMo_3$
0
20
40
60
80
100
at.% Mo